

TRANSLATION

(19) Patent Bureau of Japan (JP)

(12) Official Gazette for Unexamined Patents (A)

(11) Kokai Patent No.: Sho 59 (1984)-211036

(43) Disclosure Date: November 29, 1984

Int.Cl.³

G03C 1/68
5/00

Identification Symbols

Intrabureau No.

7267-2H

7267-2H

Request for Examination: Not Requested

Number of Inventions: 1 (Total of 5 Pages)

(54) Photopolymerizable Image-Forming Composition

(21) Application No.: Sho 58 (1983)-85625

(22) Application Date: May 16, 1983

(72) Inventors: Y. Araki

No. 36, 19-Ban, 1-Chome
Tachibana-Cho, Amazaki-City

K. Yanagisawa

11-Banchi-3, Nishiyama Waki
Yahata-City

H. Shohi

No. 79, 17-Ban, 1-Chome
Daido Minami, Higashi Yodogawa-Ku
Osaka-City

(71) Applicant: Sekisui Kagaku Kogyo K.K.

No. 4, 4-Ban, 2-Chome, Nishi Tenman
Kita-Ku, Osaka-City

Specification

[Title of Invention]

Photopolymizable Image-Forming Composition

[Claims]

1. A photopolymizable image-forming composition characterized by containing a binder consisting of a polymeric material, photopolymizable monomer or oligomer, photopolymerization initiator, reducing dye and a VI b group onium salt-type photoactivator having an optical absorption wavelength range different from the afore-mentioned photopolymerization initiator.

2. The photopolymerizable image-forming composition as described in Claim 1 in which the VI b group onium salt is a triaryl sulfonium salt.

[Detailed Description of Invention]

The present invention relates to a photopolymerizable image-forming composition.

Japanese Patent No.: Sho 59 (1984)-211036

It has hitherto been known that an image can be formed by coating the base material surface with a composition comprising a binder consisting of a polymeric material, photopolymerizable monomer or oligomer and a photopolymerization initiator, etc; exposing the coated base material surface to the light through a negative image; polymerizing or crosslinking the portion that is exposed to the light to render it insoluble in solvent and eluting the portion that is not exposed to the light. This principle is applied to production of print materials and print wiring boards.

Moreover, also known is the fact that an optical color coupler such as a leuco dye is added to the above-mentioned composition so that the light-exposed part can be clearly distinguished from the light-unexposed part thereby enabling multiple light exposure.

For instance, Japanese Examined Patent Sho 48 (1973)-38403 discloses a mixture of a leuco dye and a composition in which the imidazolyl dimer and p-aminophenyl ketone are added to an ethylenic monomer. When the U.V. light source, such as the high pressure mercury lamp generally used for the light source, is used to carry out photopolymerization or crosslinking simultaneously with optical color development in the composition, because of the presence of the dye the rate of photopolymerization or crosslinking decreases. As a result, there is a shortcoming that the exposure time must be lengthened. It is surmised that this is caused by the fact that the optical energy absorbed by the photopolymerization initiator is divided and used for both the photopolymerization or crosslinking and color development of the dye.

The present invention is made with an objective to eliminate the above-mentioned existing shortcoming, and to provide an image-forming composition which does not require a long light-exposure time because of a decrease in sensitivity caused by color development of the dye, has good photosensitivity and excellent workability, and also is suitable for multiple exposure.

Namely, the gist of the present invention lies in a photopolymerizable image-forming composition characterized by containing a binder consisting of a polymeric material, photopolymerizable monomer or oligomer, photopolymerization initiator, reducing dye and a VI b group onium salt-type photoactivator having an optical absorption wavelength range different from the afore-mentioned photopolymerization initiator.

The binder used in the present invention consists of a polymeric material; any material conventionally used as a binder of an image-forming composition can be used. For example, for the solvent development type the good solubility in solvent is important. To be specific, cited may be acetyl cellulose, acetyl butyl cellulose, polymethyl acrylate, polymethacrylic acid and methacrylic acid-methyl methacrylate copolymer.

The photopolymerizable monomer or oligomer used in the present invention refers to the material that is activated to start polymerization by irradiation of a light in the presence of a photopolymerization initiator.

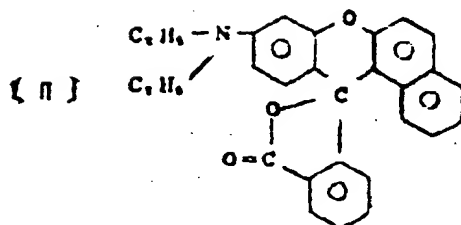
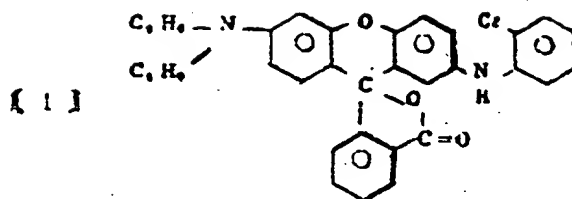
Those which have the boiling point of 100°C or higher under ambient

Japanese Patent No.: Sho 59 (1984)-211036.

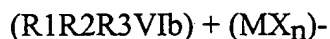
pressure, and at least one ethylene-type terminal group are used suitably. To be specific, cited may be pentaerythritol acrylate (or methacrylate), polyalkylene glycol diacrylates (or dimethacrylates) such as polyethylene glycol diacrylate (or dimethacrylate), diethylene glycol diacrylate (or dimethacrylate), triethylene glycol diacrylate (or dimethacrylate) and polymethylene diacrylate, and trimethylolpropane triacrylate (or trimethacrylate) or the oligomers derived from them. These photopolymerizable monomers or oligomers are entwined with the binder due to the photopolymerization and become insoluble, or polymerize or crosslink with the binder polymeric material having a photosensitive group to form strong images.

For the photopolymerization initiator used in the present invention, those initiators conventionally used can be used. Among them, however, the phenyl ketone type photopolymerization initiator is suitable. Cited for the specific examples of the photopolymerization initiator may be benzophenone ($\lambda_{\text{max}} = 3300 \text{ nm}$ (λ_{max} shows the wavelength of the highest peak of an optical absorption spectrum), p-aminophenyl ketone such as p, p'-bis (dimethylamino) benzophenone (henceforth, called Michler's ketone) ($\lambda_{\text{max}} = 370 \text{ nm}$), benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin butyl ether, benzoin isopropyl ether, benzyl anthraquinone, 2-methyl-anthraquinone, 2-ethyl-anthraquinone, 2-t-butyl-anthraquinone and 2-aminoanthraquinone. Many of them absorb the optical energy at the wavelength of $320 \sim 370 \text{ nm}$ and act as the photopolymerization initiator. Moreover, two types or more of these photopolymerization initiators can be mixed and used as mixtures. For instance, the wavelength of the light absorbed by the mixture of benzophenone and Michler's ketone is shifted and the efficiency of polymerization initiation due to the light irradiation is improved to result in shortening of the exposure time. Hence it is suitable.

Next, in the present invention, the combination of a reducing dye and a VI b group onium salt-type activator is used as an optical color coupler. The said photoactivator has a light absorption wavelength range different from the afore-mentioned photopolymerization initiator. Namely, the reducing dye in the present invention is oxidized by a VI b group onium salt-type activator to become the coloring type. To be specific, cited may be methyl capryl blue (colorless \rightarrow blue), toluene blue (colorless \rightarrow violet), phenyl anthranilic acid (colorless \rightarrow reddish violet), and a triarylmethane type dye of the lactone type or lactam type, or a fluoran type dye of the lactone type or lactam type; to be more specific, cited may be Crystal Violet lactone, Malachite Green lactone, rhodamine lactam and those represented by the following structural formulas I and II.

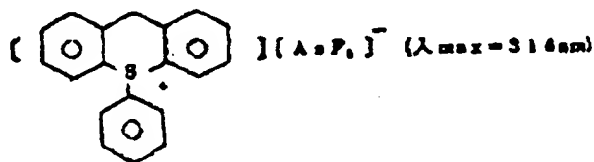


The VI b group onium salt-type photoactivators used in the present invention are the compounds as represented by the following general formula.



(wherein R1, R1 and R3 represent the aryl groups, VI b represents a periodic table VI b group element selected from sulfur, selenium and tellurium, M represents an element selected from transition metals, rare earth elements, lanthanoids, actinoids and semimetals such as B, P and As, X is a halogen and n represents an integer of 1 ~ 6). For the complex anion in the formula there are BF₄⁻, PF₆⁻, SbF₆⁻, FeCl₄⁻, SnCl₆²⁻, SbCl₆²⁻, BiCl₅²⁻, AlF₆³⁻ and GaCl₄⁻.

For the specific example of these VI b group onium salt optical activators the following may be cited. Namely, triphenylsulfonium hexafluoroarsenate ($\lambda_{\max} = 298 \text{ nm}$) (λ_{\max} represents the wavelength of the highest peak of an optical absorption spectrum); tris (4-totoxyphenyl (typographical error?)) sulfonium hexafluoroarsenate ($\lambda_{\max} = 280 \text{ nm}$), diphenyl-2, 5-dimethylphenylsulfonium hexafluoroarsenate ($\lambda_{\max} = 307 \text{ nm}$), tris (4-methylphenyl)sulfonium fluoroborate ($\lambda_{\max} = 278 \text{ nm}$) or



These Vb group onium salts are used by selecting those which have an optical absorption wavelength range different from the afore-mentioned

photopolymerization initiator. The difference between two optical absorption wavelength ranges is generally about 20 nm or more in terms of the difference of the wavelength showing the highest peak of an absorption spectrum. However, the difference of the highest peaks of the absorption spectra of the above-mentioned photoactivator and photopolymerization initiator may also be 10 nm. Conversely, when both distributions are broad, since 500 nm or more is required, the absorption peak wavelength and distribution are taken into consideration, and the wavelength range difference between the two substances must be such that the light whose wavelength is mainly absorbed by the afore-mentioned photopolymerization initiator activates the above-mentioned photoactivator to allow it to function as an oxidizer and is also utilized for color development of the above-mentioned reducing dye, and does not substantially inhibit the polymerization and curing of the composition. As to the preparation of the above-mentioned VI b group onium salt, it is described in detail in J. Am. Chem. Soc. 91, 145 (1969) and J. Org. Chem. 35, No. 8, 2332 (1970). The VI b group onium salt-type activator used in the present invention is different from other photoactivators for reducing dyes in that there is no possibility of generation of foams or of decomposition when stored at room temperature over an extended period of time; it excels in the long-term quality stability.

When the composition of the present invention is used by laminating it on the copper-clad laminate to which a thin copper foil is adhered, an adhesion promotor may be used in order to improve the adhesion. Moreover, a thermal polymerization inhibitor, plasticizer and flame retardant may be added as needed.

In order to obtain the composition of the present invention, it is sufficient to combine and uniformly mix the above-mentioned binder consisting of a polymeric material, photopolymerizable monomer or oligomer, photopolymerization initiator, reducing dye and the afore-mentioned VI b group onium salt-type photoactivator having an optical absorption wavelength range different from the photopolymerization initiator, and furthermore, if needed, an adhesion promotor may be added. Since, for the application, usually a thin film is formed on the surface of the base material such as a synthetic resin, it is preferable that the composition be a liquid composition which can be mixed with methyl ethyl ketone and other appropriate solvents to form a viscosity that enables it to be coated on the base material, and can also be dried upon volatilization of the solvent. Moreover, as to the quantitative relationship of the components of the above-mentioned composition, the recommended proportion is 10 ~ 300 parts by weight of a photopolymerizable monomer or oligomer, 0.1 ~ 20 parts by weight of a photopolymerization initiator, 0.01 ~ 10 parts by weight of a reducing agent and 0.001 ~ 2 parts by weight of a VI b group onium salt photoactivator per 100 parts by weight of a binder consisting of a polymeric material.

The composition of the present invention is used for the preparation of relief print plates and the application of photo resists. Usually the solution in which the composition of the present invention is dissolved in solvent is coated on a transparent sheet-shaped base material and dried and, if necessary, a protective film is formed on it. Then, if necessary, the protective film is removed, and the composition is laminated with heat fusion on a member to form an image such as a photoresist image, for example, on the surface of a copper-clad laminate to which a thin copper foil is adhered; it is followed by irradiation of active light from above through a negative film to expose the exposed part to the light. Afterward, if necessary, the transparent sheet-shaped base material is peeled off and the unexposed part is removed with solvent to carry out development. Henceforth the unprotected part of the surface (the part in which the composition of the present invention is removed with solvent) is subject to the treatment of etching or metal plating. The exposed part of the composition of the present invention develops color by the photoactivation-oxidation of the reducing dye with the VI b group onium salt-type photoactivator contained in the composition. Therefore, it is easy to distinguish the exposed part from the unexposed part in the exposure process; thus it is very convenient when multiple exposure is performed or at the time of confirming the state of exposure.

Furthermore, the optical color coupler of the combination of a reducing dye and a VI b group onium salt-type photoactivator in the composition of the present invention is excellent in the color stability without the disappearance of the colored image in a short time after exposure, and its workability is improved.

Moreover, when a leuco dye type color coupler is used conventionally, it is surmised that, because the irradiated light energy is divided into two parts, namely, the polymerization or crosslinking of the composition and color development, the rate of polymerization-curing of the composition decreases thereby requiring a long exposure time. As compared to this, in the composition of the present invention there is no such shortcoming, a short-time exposure is sufficient, and the exposure workability is also excellent.

[Example 1]

Polymethyl methacrylate (MW = 2.0×10^5)	60 g
Trimethylolpropane triacrylate	33 g
Benzophenone	3.51 g
Michler's ketone	1.51 g
Crystal Violet lactone	1.0 g
Triphenylsulfonium hexafluoroarsenate	0.1 g

The above compounds were dissolved in methyl ethyl ketone to make a solution of 300 g in total weight. This solution was coated on a polyethylene terephthalate film support so as to form a 50 μm thickness after drying. After the coated film was dried it was laminated on a glass fiber-reinforced

Japanese Patent No.: Sho 59 (1984)-211036

epoxy resin plate, which had been coated with copper at 115°C, so as to allow the above-mentioned film to contact with the copper surface.

Subsequently, the above-mentioned photosensitive laminated plate was subject to the exposure of 90 millijoule (Mj) in a vacuum frame at a location at a distance 1 m apart from the 400 W high pressure mercury lamp through a negative image for testing (21 $\sqrt{2}$ step exposure step guide = the negative image gradually becomes deep by every $\sqrt{2}$ at 21 steps from the transparent state) and a negative image for printed wiring circuits which was arranged so as not to overlap with it. The exposure time was 20 sec. After the exposure, the polyethylene terephthalate film support was peeled off and the exposed layer was immersed in 1, 1, 1-trichloroethane (to remove the unexposed part) for development and dried. In the image by the negative image for testing, the 9th step image remains in the glass fiber reinforced epoxy resin plate coated with copper. Moreover, the resolution in the image for the printed wiring was 50 μm . Moreover, prior to the above-mentioned development, the unexposed part was colorless, the exposed part was clearly colored purple, and color development absorbance 0.5 contrast was sharp and was sufficient for carrying out an exposure inspection. Furthermore, after this exposure it was left standing overnight. On the following day, after development, etching was carried out, and the coating was removed to form a printed circuit. Nevertheless, the clear color remained in the exposed part up to the step of the coating removal; thus it was convenient to carry out the inspection on the states of development, etching and coating removal.

[Example 2] Used for the reducing dye was rhodamine lactam in place of Crystal Violet lactone, and for the VI b group onium salt-type photoactivator was diphenyl 2,5-dimethylphenylsulfonium hexafluoroarsenate in place of triphenylsulfonium hexafluoroarsenate. Otherwise, the developments of the negative image for testing and negative image for printed wirings, and the formation of printed wirings were carried out in the same way as Example 1.

As a result, it was found that each of the extent of curing of the exposed part, resolution and the extent of color development was the same as Example 1.

[Comparative Examples 1 ~ 4]

The compositions as shown in the following table were used to carry out the exposure, development and formation of printed circuits in the same way as Example 1. The results are shown in the following table.

BEST AVAILABLE COPY

	Comparative Example			
	1	2	3	4
Polymethyl methacrylate	609	60	60	60
Trimethylolpropane triacrylate	339	33	33	33
Benzophenone	159	15	15	0
Michler's ketone	159	15	0	15
Imidazolyl dimer note 1)	0	1	1	1
Leuco Crystal Violet	0	1	1	1
Extent of curing at the time of 90 mJ/cm ² irradiation note 2)	9 Steps	5	2	1
Color development absorbance	0	0.3	0.3	0.3
Resolution note 3)	50 μ m	200	200 <	200 <

Note 1) 2-(o-chlorophenyl)-4,5-dimethoxyphenyl-imidazolyl dimer

Note 2) In the same way as Example 1, it indicates the number of steps that remain in the photopolymerization in the image in the negative image for testing.

Note 3) It indicates that Comparative Examples 3 and 4 have values greater than 200 μ m, and it shows poor resolution.

Translation: Language Services
C & G Associates
May 4, 2001